Synthesis of Co(OH)$_2$/USY composite and its application for electrochemical supercapacitors

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Abstract

A novel composite of Co(OH)$_2$ and ultrastable Y molecular sieves was synthesized with an improved chemical precipitation method. The Co(OH)$_2$/USY composite and its microstructure were characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM) and Fourier transform infrared (FTIR). Co(OH)$_2$/USY microstructure applied for the electrochemical energy storage displayed superior capacitive performance. Upon annealing at 100 °C, the maximum specific capacitance was up to 958 F/g, which was comparable to that of hydrated ruthenium oxide. Higher annealing temperatures larger than 100 °C only resulted in a decline of the specific capacitance.
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1. Introduction

Recently, supercapacitors draw increasing attention in the areas of electric energy storage systems because supercapacitors possess many advantages over the second battery and conventional capacitors [1]. In particular, the power density of supercapacitors is the most attractive property. However, the lower energy density of supercapacitors compared to that of secondary battery is a drawback for practical devices such as electric vehicles [1]. From the application point of view, it is necessary to develop supercapacitors with high energy density. It is well established that the energy density is given by $Cv^2/2m$ where v is the initial voltage, and C the specific capacitance [2]. Obviously, maximizing the capacitance of the electrode materials is the key to increase the energy density.

It is well known that hydrated ruthenium oxide is an excellent material with remarkable high specific capacitance values ranging from 720 to 760 F/g (for single electrode system) [3,4]. However, the high cost of raw materials and iridium precursors has prevented this material from commercial applications [5]. As a result, cheaper candidates with good capacitive characteristics have attracted many efforts.

Transition metal oxides and hydroxides are promising candidates applicable in supercapacitors. For example, nickel oxide or nickel hydroxide synthesized with sol–gel or electrochemical methods have shown a specific capacitance of 200–300 F/g [6,7].

In this paper we synthesized a novel composite of Co(OH)$_2$ and ultrastable Y molecular sieves (denoted as Co(OH)$_2$/USY) with an improved chemical precipitation method. The goal of this work is to use this novel composite as the electrode material for electrochemical supercapacitors. Electrochemical studies showed that the composite electrode has superior capacitive performance, and the maximum specific capacitance is up to 958 F/g (for single electrode system), which is comparable to that of hydrated ruthenium oxide. In addition, we also studied the effect of annealing temperatures on the capacitance property of Co(OH)$_2$/USY composite.

2. Experimental

2.1. Composite synthesis

Ultrastable Y molecular sieves was synthesized by repeated sodium exchange of zeolite NaY (LZPCC, Si/Al = 2.3), with aqueous solution of NH$_4$NO$_3$ at 35 °C for 14 h followed by steaming at 650 °C for 3 h.

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Thirty milliliter aqueous solution of $NH_3 \cdot H_2O$ (5 ml, 25–28 wt.%) was added dropwise to the mixed aqueous solution of $CoCl_2 \cdot 6H_2O$ (0.0126 M, 24.79 wt.%), and the same weight of USY with vigorous magnetic stirring until a dark green precipitation of $Co(OH)_2$/USY composite was formed. The final pH was adjusted to be around 8.5. Then, the resulting precipitate was filtered using a centrifugal filtration method and washed with distilled water and ethanol several times. The final product was divided into seven portions and heated from 100 to 450 °C without air for 3 h. In addition to the composite, pure $Co(OH)_2$ was prepared following the same procedure.

2.2. Synthesis of Co(OH)₂/USY composite electrodes

The working electrodes (12.5 mg) were prepared by mixing 80 wt.% of $Co(OH)_2$/USY composite powder with 7.5 wt.% of acetylene black (>99.9%), 7.5 wt.% of conducting graphite and 5 wt.% of poly (tetrafluoroethylene) dried powder (PTFE). The first three components were mixed together in an agate mortar until homogeneous black powder was achieved. PTFE was then added to the mixture with a few drops of ethanol. The synthesized paste was pressed at 20 MPa to a nickel gauze with nickel wire leading for connection, and dried for 1h under vacuum at room temperature. The surface area of $Co(OH)_2$/USY composite electrode was about $1 \, cm^2$.

2.3. Characterization of the materials and electrodes

Electrochemical studies were carried out using an electrochemical working station (CHI-660, Chenhua, Shanghai). A platinum gauze and a saturated calomel electrode (SCE) were used as a counter electrode and reference electrode, respectively. Cyclic voltammogram was collected by polarizing the working electrode between −0.20 and 0.60 V in 1 M KOH aqueous solution. TEM (JEDL-2010 model) and SEM (JSM5600LV, JOEL) were employed to examine the morphology of $Co(OH)_2$/USY composite. FTIR spectra were recorded with a model 360 Nicolet AVATAR FTIR spectrophotometer.

3. Results and discussion

3.1. Analysis of Co(OH)₂/USY composite

Fig. 1 displays TEM and SEM images of pure USY and the synthesized composite. Pure USY particles, with the average particle diameter about 800 nm, show regular morphology with good dispersion. The present images illustrate that there is a fundamental morphology change from pure USY particles to loaded with $Co(OH)_2$. TEM images show that amount of swelling fibered $Co(OH)_2$ have grown on the outer surface of the USY matrix. It is noteworthy that the fibered compound shows highly dispersed morphology and a loosely packed microstructure in the nanometer scale.

To characterize the $Co(OH)_2$/USY composite material, we employed FTIR spectroscopy, which is sensitive to short-range order in a compound. Fig. 2 shows the spectrum of pure $Co(OH)_2$ with strong peaks at 3628, 490, 440 cm^{-1}, which correspond to the free non-hydrogen bonded OH group and Co–O stretching frequencies, respectively. Our
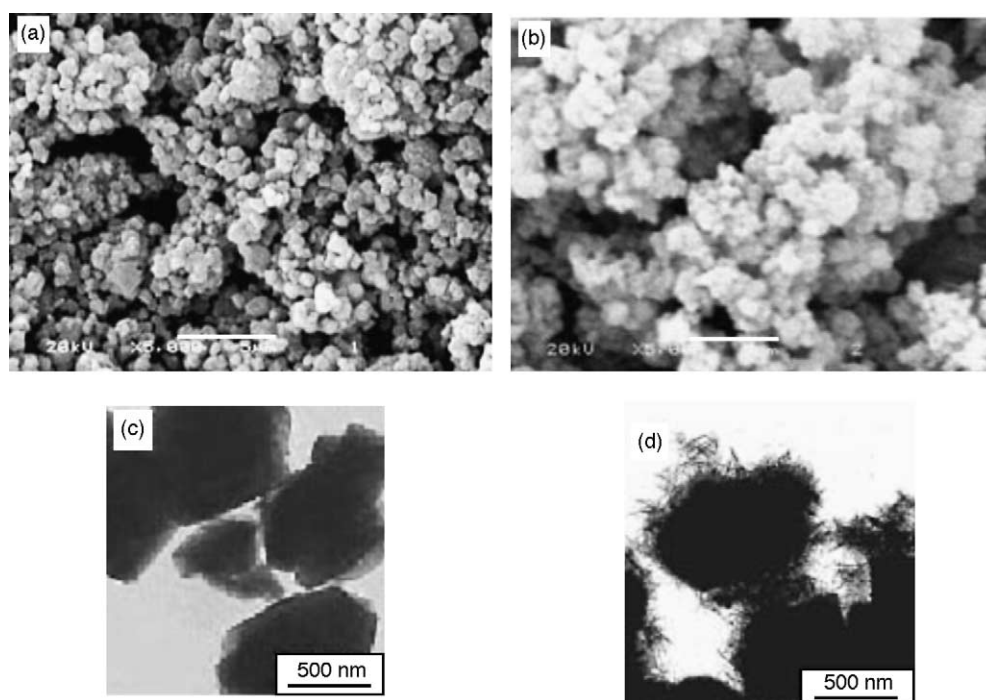

Fig. 1. SEM and TEM images of pure USY and $Co(OH)_2$/USY composite: (a) and (c) pure USY; (b) and (d) $Co(OH)_2$/USY composite with 28.1 wt.% $Co(OH)_2$ loading.
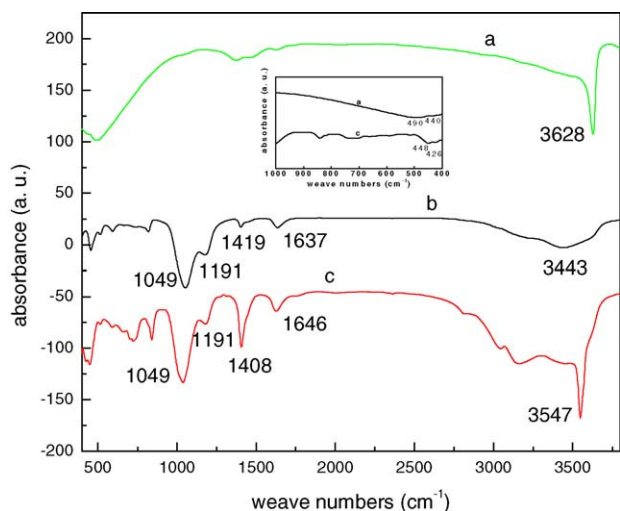
Fig. 2. FTIR spectra of pure $Co(OH)_2$, pure USY and composite: (a) pure $Co(OH)_2$; (b) pure USY; (c) $Co(OH)_2$/USY composite with 28.1 wt.% $Co(OH)_2$ loading.

Fig. 3. Cyclic voltammetric (CV) curve for $Co(OH)_2$/USY composite electrode in 1 M KOH. Cyclic voltammetric curve at 5 mV/s.

experimental results are in good agreement with those reported by Elumalia et al. [8]. The pure USY compound exhibits a broad peak at 3443 cm^{-1} showing the associating OH stretching frequency. For the $Co(OH)_2$/USY composite, the OH group frequency was shifted from 3628 to 3547 cm^{-1} and corresponding Co–O stretching mode was also shifted from 490 to 448 and from 440 to 426 cm^{-1}, respectively. Furthermore, the pronounced broad peak was split, associated with the OH group. The shifted and split characteristic peak suggests a strong physical and/or chemical interaction between the USY and $Co(OH)_2$. Work in progress will be attempted to investigate the growth mechanism for $Co(OH)_2$ on the surface of the USY.

3.2. Electrochemical properties

To evaluate the microstructure of the synthesized $Co(OH)_2$/USY composite and its electrochemical property, we use this material to fabricate the electrode of supercapacitors. The composite electrode was characterized with cyclic voltammograms and chronopotentiometric measurements. The open-circuit potential of $Co(OH)_2$/USY composite electrode is about -0.20 V in 1 M KOH aqueous solution. Fig. 3 shows that the characteristic of the capacitance is very different from that of the electric double-layer capacitance, in which the CV curve is close to the ideal rectangular shape. The present results imply that the measured capacitance is mainly associated with the redox mechanism. The two strong redox reaction peaks are responsible for the very high capacitance. Based on the average value of peak potential of p_1 versus p_2 and p_3 versus p_4, peak p_1 is due to the oxidation of $Co(OH)_2$ to CoOOH and peak p_2 is for the reverse process; peak p_3 is due to oxidation CoOOH to CoO_2 and peak p_4 is therefore attributed to the reduction of CoO_2 to CoOOH. The potential difference of p_1 and p_2 is
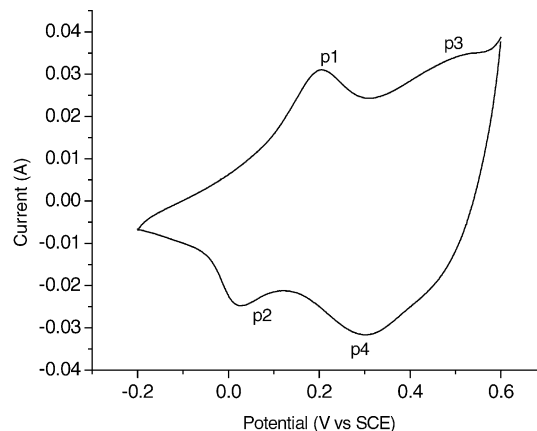
larger than 0.20 V, which is higher than the theoretic ΔE_p value of 0.058 V for a reversible single-electron transfer process. Therefore, it is suggested that this reaction occurs as a quasi-reversible process during the anodic potential sweep of the $Co(OH)_2$.

Fig. 4 shows the charge–discharge behavior of the composite electrode. The shape of the discharge curve does not show the characteristic of pure double layer capacitor or pure supercapacitor, in agreement with the result of the CV curve. The specific capacitance is calculated from Eq. (1):

$$C = \frac{I\Delta t}{m\Delta v} \qquad (1)$$

with I being the discharge current, m the mass of the composite, Δv the potential drop during discharging, Δt the total discharge time, and C the specific capacitance. Based on Eq. (1), the specific capacitance of $Co(OH)_2$/USY from Fig. 4 is 958 F/g. The capacitive performance of the $Co(OH)_2$/USY composite is about 10 times higher than pure $Co(OH)_2$

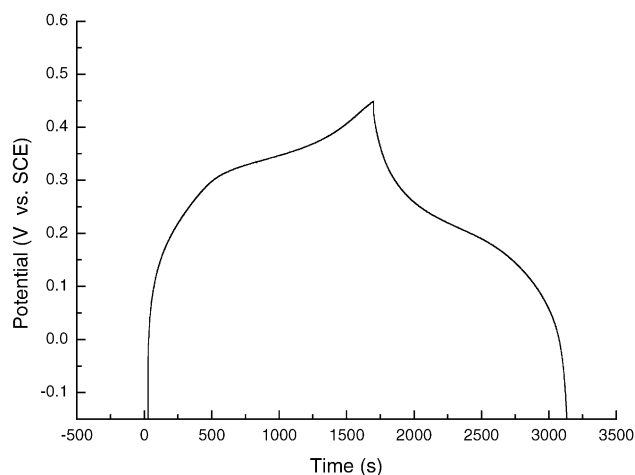Fig. 4. Charging–discharging behavior of $Co(OH)_2$/USY composite electrode in 1 M KOH with a potential window of -0.15 to 0.45 V vs. SCE. Discharging curve at 4 mA.
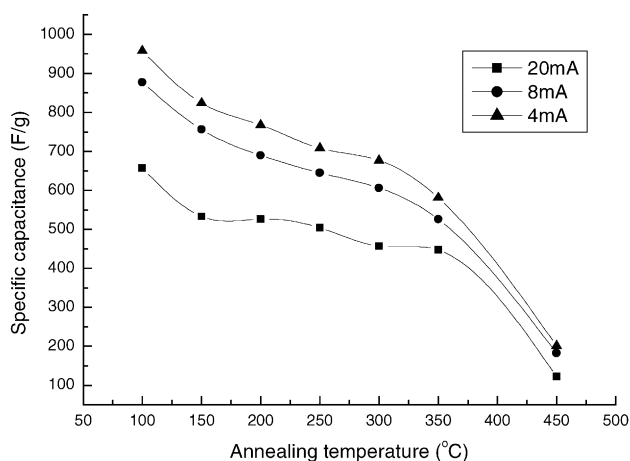
Fig. 5. The specific capacitance of Co(OH)$_2$/USY composite electrode as a function of annealing temperature with different discharge currents.

Fig. 6. Charging–discharging behavior of Co(OH)$_2$/USY composite electrode in 1 M KOH. Discharging curve at 4 mA.

prepared with the same procedure, and comparable to that of hydrate ruthenium oxide at alkaline electrolyte [3,4]. Obviously, Co(OH)$_2$/USY active electrode exhibits excellent capacitive characteristic, and its specific capacitance of Co(OH)$_2$ is up to 3409 F/g (28.1 wt.% Co(OH)$_2$), approximately 98% of the theoretical value, 3458 F/g for Co(OH)$_2$ [9]. The present work demonstrate that Co(OH)$_2$ has been well dispersed on the surface of USY matrix and can effectively be charged and discharged in experimental power density.

Based on the above discussions, we propose that the molecular sieves play a critical role in optimizing superior capacitive performance of Co(OH)$_2$/USY composite. The USY offers a nanometer template for formation of swelling fibered Co(OH)$_2$ that is highly dispersed in three-dimensional (3D) space. The highly dispersed compound exhibits both very high surface area and nano-scale microstructure. The superior capacitive characteristic is attributed to the high-dispersed capability of USY towards to Co(OH)$_2$.

Fig. 5 shows the effect of annealing temperature on the capacitive properties of the Co(OH)$_2$/USY composite electrodes. With increasing annealing temperature, the decline tendency of the specific capacitance is similar and irrelevant to different discharge currents. As low as 350 °C, moderate specific capacitance of 581 F/g was obtained for the same discharge rate. We suggest that the Co(OH)$_2$ of the composite was well attached to the surface of USY, as a result, it is more difficult to aggregate for higher annealing temperature. Thus, we also present here a new synthesis technique that can overcome aggregation to some extent.
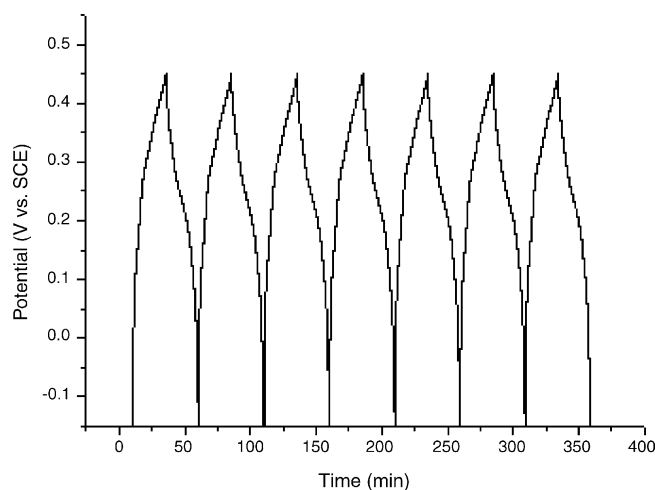
The decreasing ratio is similar irrelevant to the different annealing temperatures. As discharge current increases, the large voltage (IR) drop produces, and finally the capacitance decreases. Thus, the specific capacitance obtained at the smallest discharge current of 4 mA is supposed to be close that of full utilization of the materials.

The stability of the active material in 1 M KOH electrolyte was examined by chronopotentiometry. Fig. 6 shows approximately 4% loss of capacitance after 1000 consecutive cycles, implying that very stable Co(OH)$_2$/USY composite is a better electrode material for redox supercapacitors.

In conclusion, we have synthesized a novel Co(OH)$_2$/USY composite, and applied its microstructure for electrochemical supercapacitors. The special microstructure can accommodate the electroactive species in the solid bulk electrode material. The composite electrode shows great potential as the electrochemical supercapacitors.

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